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STUDY ON THE CHEMICAL CHARACTERISTICS OF POLLUTING FOG IN GUANGZHOU AREA IN SPRING

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Abstract: Samples of fog water collected in the area of Guangzhou during February, March and April of 2005 are used in this work to study the chemical composition of fog water in polluting fog there. Three typical episodes of polluting fog are analyzed in terms of ionic concentration and their possible sources. It is found that the concentration of various ions in fog water is much higher than those in rainwater. Fog not only blocks visual range but contains liquid particles that result in high degree of pollution and are very harmful to human health. $SO_4^=$ is the anion with the highest concentration in fog water, followed by NO_3^-. For the cation, Ca^{++} and NH_4^+ are the highest in concentration. It is then known that rainwater is more acidic than fog water, indicating that ionic concentration of fog water is much higher than that of rainwater, but there are much more buffering materials in fog water, like NH_4^+ and Ca^{++}. There is significant enrichment of Ca^{++}, $SO_4^=$, and Mg^{++} in fog water. In the Guangzhou area, fog water from polluting fog is mainly influenced continental environment and human activity. The episodes of serious fog pollution during the time have immediate relationships with the presence of abundant water vapor and large amount of polluting aerosol particles.

Key words: Atmospheric chemistry; polluting fog; fog water; chemical composition; Guangzhou

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1 INTRODUCTION

Fog is an aerosol system made up of a large number of minute water droplets or ice crystals that are suspended in the air near the ground surface, a product from the condensation or subclimation in this particular layer of the atmosphere. With the diameter around 10 μm on average and the maximum no more than 50 μm normally, these water droplets intensely scatter visible light so as to cause vision barrier. Fog can be of radiation, advection or frontal surface when classified by the mechanism of generation. The presence of fog greatly reduces the transparency of the air, worsens the visibility and endangers traffic transportation [1]. A long puzzle since old, old times for mankind, fog has been a traditional subject of contemporary international research.

Ever since the first scientific study on radiation fog by Taylor in early 20th century [2], a large number of field experiments have been conducted overseas for more than 30 years. Extensive observational fog studies were carried out in the Chemung River Valley near Elmira, N.Y.C [3] and Albany, N.Y. [4], USA in 1970, Cardington, Bedfordshire in Britain [5] in 1971, and Po Valley in Italy [6] in 1989. As fog forms near the ground surface where people live their everyday life, the urban fog is much different from what it used to be in the past, because of the increasing effect of human activity. It is mainly reflected in the increase of

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pollutants and the decrease of liquid-state water content. While called dust fog, smog or dry fog by some researchers, the urban fog is best dabbed "polluting fog", which is what we think a more appropriate name, because of its highly toxic hazards for human health, which has not been much worked on or reported as it should [1]. It is the purpose of this study to try to learn just how high the concentration of pollutants could be in fog water by using valuable, hard-to-have-access-to urban fog water samples. There have been several large-scale research projects on fog over the past 20 years, such as those on radiation fog in Chongqing in 1984 – 1990 [7, 8] and Sishuangbanna [9] in 1987 and on advection fog in Nan Ling Mts. that is high above sea level and closely associated with the activity of a quasi-stationary front in South China [10]. Besides, a number of other observational experiments and studies were also conducted in China [11 - 16]; most of them were mainly about fog's macro- and micro-physical structures but few touches upon the chemical composition of fog water, except for Chongqing, Lushan Mt., southern Fujian province, Dayaoshan of Nan Ling Mts., Shanghai and Sishuangbanna [7, 8; 16 - 20]; and Chongqing and Shanghai are the two cities that were ever studied for the composition of polluting fog in urban environment. Differences are bound to occur in the physical and chemical characteristics, generation and development processes and temporal and spatial distribution of fog with different nature and location. Additionally, heavy fog only happens at moderate frequency and it is difficult to collect fog water, especially so in urban areas where it is extremely difficult to successfully gather samples sufficient enough for composition analysis. Over the course of five years, only three samples collected in 2005 were qualified to conduct composition analysis with. The chemical characteristics of the fog water in Guangzhou's polluting fog will be studied and discussed here in this study.

2 BASIC BRIEFING ON THE OBSERVATION AND WEATHER BACKGROUND

The samples were gathered on top of a 21-storey office building (82 m above sea level) of Guangdong Meteorological Bureau, which is located in downtown Guangzhou Municipal (23°07.854′N, 113°17.845′E). For a total of three heavy fogs that were measured over seven typical foggy days, three samples of fog water and nine samples of rainwater were collected. For details of the collection and rinsing of the samples and of the determination of composition, see Wu et al.[18].

The sampling began on Feb. 25, and ended on Mar. 30, 2005, which coincided with a time of frequent frontal activity in the area of Guangzhou when warm and humid air flow was active and usually persistent for two to three days before the passage of cold air, resulting in low visibility. In a case for Feb. 25, visibility was very low throughout the day with the minimum at 380 m only and humidity as high as near saturation. After the front passed through, precipitation usually followed, leading to the improvement of visibility. A total of three such typical episodes were recorded over the time of study. Very low in the content of water, the fog in Guangzhou is also very dark and thick somewhat like ink (Fig.1).

Fig.1 Contrasts between fog water sampled from the polluting fog in Guangzhou (as shown in the left bottle) and rainwater (as shown in the right bottle) for the same period.

3 ANALYSIS

Table 1 lists the chemical characteristics of fog water for the three episodes of polluting fog. It shows that the pH value is all lower than the existing standard for acid rain (with pH＜5.6 and maximum at 5.85 only), suggesting serious hazards from both acid rain and acid fog in the spring of Guangzhou. As shown in the list of electrical conductivity in the table, the general concentration of ions in the fog water is rather high. The distribution of fog's ionic concentration differs much between the fog episodes and so does the chemical composition of rainwater samples collected during the same time. The equivalence ratio is at a balanced state between the positive and negative ions.

As shown in Table 2, the ionic composition of fog water is high in both the concentration and dominant composition regardless of the location; for Guangzhou, it is between 10 to over 100 times more than that for Nan Ling Mts., Lu Shan Mt. and southern Fujian, a fact that has much to do with the presence of serious air pollution in the metropolitan districts. In the fog water of Guangzhou, $SO_4^{=}$ and Ca^{++} are among the ionic compositions that have the highest concentration;

and the apparently high concentration of Ca^{++} is possibly due to the serious effect of dust from building sites or some other industrial sources. The ionic presence of the soluble Ca^{++} in aerosol results from its direct emission and some processes may be working to enable it to enter the liquid phase during the hygroscopic growth of aerosol. In addition, more Ca^{++} is present in the liquid phase in fog water than in rainwater, mainly because of the enrichment effect.

The polluting fogs recorded were caused by serious local aerosol pollution in the Guangzhou area. As the aerosol pollution and atmospheric transparency are getting increasingly worse in the surrounding areas and aerosol clouds can appear all year round, visibility and air quality are decreasing. It is indicated that the change has reflected human activity, economic development and significant regional characteristics [21]. Fig.2 presents the distribution diagram of the diurnal mean concentration of black carbon (BC) as measured with an aethalometer (Magee Scientific AE-31) at an atmospheric composition watch station in Panyu, Guangzhou. The much higher concentration of BC aerosol for the period of heavy fog is related to the presence of high energy consumption, numerous discharge sources from processing industries, dense regional traffic network and particular meteorological condition in Guangzhou and surrounding urbanized areas. The serious polluting fog observed in Guangzhou during this time was directly related with the local presence of sufficient amount of water vapor and large amount of polluted particles of aerosol.

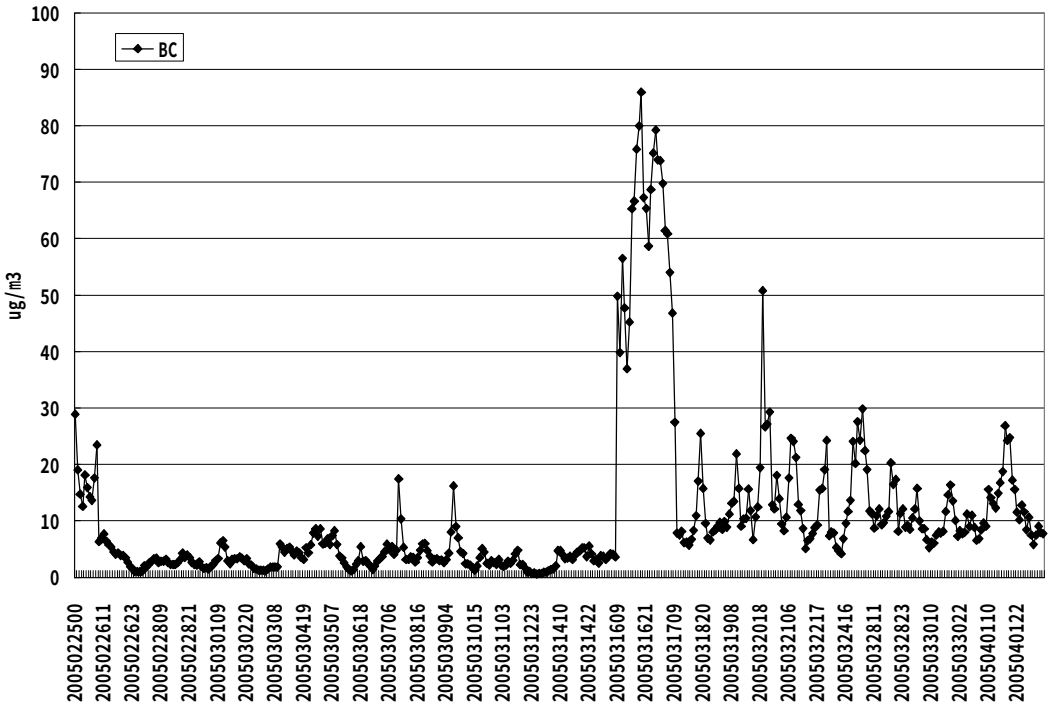

Fig.2 BC aerosol concentrations for Feb. 25 – Apr. 2005 observed at the atmospheric composition station in Panyu, Guangzhou.

Table 1 Chemical characteristics of fog water of the three polluting fogs in Guangzhou. (unit of concentration: μmol/l)

Process/time	Sampling time/h	pH	conductivity/(μS/cm)	F^-	Cl^-	NO_3^-	$SO_4^=$	NH_4^+	K^+	Na^+	Ca^{++}	Mg^{++}
Feb. 25 – 26	24	5.35	5800	1341	2750	6407	35421	10024	447	2631	5584	512
Mar. 16 – 18	60	5.75	5400	3083	31283	33915	25565	4935	2612	19313	26863	3788
Mar. 29 – 30	36	5.85	280	235	1487	1331	1197	359	154	1204	1725	268
Mean		5.65	3826	1553	11840	13884	20727	5106	1071	7716	11391	1523

Table 2 Chemical characteristics of fog water of different locations. (unit of concentration: μmol/l)

Location	time/year	pH	F^-	Cl^-	NO_3^-	$SO_4^=$	NH_4^+	K^+	Na^+	Ca^{++}	Mg^{++}
Guangzhou	2005	5.6	1553	11840	13884	20727	5106	1071	7716	11391	1523
Lushan Mt.[16]	1987	5.4	9	26	73	220	323	14	19	106	13
Southern Fujian[17]	1993	3.6	29	214	257	395	469	91	344	149	53
Nan Ling Mts.[18]	1999 - 2001	5.5	34	44	97	679	531	134	59	611	21

4 COMPARATIVE ANALYSIS OF CHEMICAL COMPOSITION BETWEEN FOG WATER AND RAINWATER

During the sampling period for fog water from Feb. 27 to Mar. 30, a total of nine items of rainwater samples were collected. As shown in Table 3, the ionic concentration is much higher in fog water than in rainwater; fog not only causes vision barrier but also is composed of particles that are highly polluted and very hazardous to the health of human beings. Respiratory diseases can be easily inflicted when such fog happens [1].

It is also shown in Table 3 that Guangzhou is similar to Nan Ling Mts. And Lushan Mt. in terms of the fact that the ionic concentration is much higher in fog water than in rainwater, suggesting the presence of large amount of polluted substance resolved in fog water, which is directly related with the local condition of atmospheric pollution. As the high level of ionic concentration is favorable for the formation and persistence of fog droplets, the fog damage is made worse. The cases for the three locations have become a great contrast, reflecting the diversity of ionic concentration distribution in fog water, which is related to both the formation and environment of fog. In addition, rainwater is more acidic than fog water, which is true for Guangzhou, Nan Ling Mts. and Lu Shan Mt. [22]. It indicates that more buffer substances exist in the abundant ionic compositions, like NH_4^+ and Ca^{++}, though the ionic concentration is much higher in fog water than in rainwater.

Table 3 Comparison of the observations of water-soluble ionic compositions in the rainwater and fog water of Guangzhou and those of Nan Ling Mts. and Lu Shan Mt.(μmol/l)

Site	Sample	pH	*D*/(μS/cm)	F^-	Cl^-	NO_3^-	$SO_4^=$	NH_4^+	K^+	Na^+	Ca^{++}	Mg^{++}
Guangzhou	Rain water	4.2	42	18	45	109	246	224	8	23	169	12
	Fog water	5.6	3826	1553	11840	13884	20727	5106	1071	7716	11391	1523
Nan Ling [18]	Rain water	4.7	22	3	14	8	59	45	18	14	46	3
	Fog water	5.5	162	34	44	97	679	531	134	59	611	21
Lu Shan[16]	Rain water	4.9		1	12	12	23	67	20	4	11	1
	Fog water	5.4		9	26	74	220	323	15	19	107	13

It is known from an analysis of enrichment factors that take as the frame of reference the surface layer of lateritic red soil in South China [23], the degree of ionic content enrichment differs between the observed episodes of fog (Table omitted). The difference in the most enriched chemical composition for the three episodes of pollution shows that the source of principal pollution varies between them, suggesting that meteorological difference probably be a possible important factor in causing the variation of relative contribution by polluting sources. It is based on this assumption that the backward trajectory analysis will be used to infer the distribution and contribution of polluting sources (figure not shown).

It is shown in the percentage of non-sea-salt composition in the fog water of Guangzhou (Table omitted) that, the fog water in the three fog episodes during the spring of 2005 was mainly influenced by continental environment and human activity and mildly by marine environment, which is in contrast to the case of heavy fog in Nan Ling Mts. where human activity and continental environment are the two dominant factors [18].

For analyses of other aspects, refer to the Chinese edition of the journal.

5 SUMMARY AND DISCUSSIONS

(1) Polluting fog is a hazard that cannot be ignored because of the relatively low pH value in its

fog water.

(2) For the anion, $SO_4^{=}$ has the highest concentration, followed by NO_3^- and Cl^-; for the cation, however, the order is Ca^{++}, Na^+ and NH_4^+.

(3) The ionic concentration is much higher in fog water than in rainwater. Rain water is more acidic than fog water, indicating that more buffer substances exist in the abundant ionic compositions, like NH_4^+ and Ca^{++}, though the ionic concentration is much higher in fog water than in rainwater.

(4) Related with the structure and generating mechanism of fog and environmental factors, chemical characteristics of fog water vary from one episode of fog to another. The difference in meteorological condition may be an important factor that causes the variation of the relative contribution by polluting sources. As shown in the airflow trajectory analysis, the transportation between various polluting sources can be one of the important causes.

(5) Differences exist in the degree of enrichment of ionic concentration between different fog episodes. The three fog episodes in the spring of 2005 were mainly affected by continental environment and human activity, though the marine environment also contributed to it in some extent.

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